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METHOD FOR MANUFACTURING AROMATIC CARBONIC ACID ESTER

Inventors:

Yuji Okago
Tsukuba Research Lab.,
Mitsubishi Chemical
Industries, Ltd.
8-3-1 Chuo, Ami-machi,
Inashiki-gun,
Ibaraki-ken

Hidehito Hayashi
Tsukuba Research Lab.,
Mitsubishi Chemical
Industries, Ltd.
8-3-1 Chuo, Ami-machi,
Inashiki-gun,
Ibaraki-ken

Hidekazu Miyashiro
Tsukuba Research Lab.,
Mitsubishi Chemical
Industries, Ltd.
8-3-1 Chuo, Ami-machi,
Inashiki-gun,
Ibaraki-ken

Katsufumi Kujira
Tsukuba Research Lab.,
Mitsubishi Chemical
Industries, Ltd.
8-3-1 Chuo, Ami-machi,
Inashiki-gun,
Ibaraki-ken

Masatoshi Takaki
Tsukuba Research Lab.,
Mitsubishi Chemical
Industries, Ltd.
8-3-1 Chuo, Ami-machi,
Inashiki-gun,
Ibaraki-ken

Naoki Suzuki
Tsukuba Research Lab.,
Mitsubishi Chemical
Industries, Ltd.
8-3-1 Chuo, Ami-machi,
Inashiki-gun,
Ibaraki-ken

Applicant:

000005968
Mitsubishi Chemical
Industries, Ltd.
2-5-2 Marunouchi,
Chiyoda-ku, Tokyo

Agent:

Akish Hasegawa, patent
attorney

[There are no amendments to this patent.]

Abstract

Objective

The purpose of this invention is to provide an industrially preferable method for manufacturing an aromatic ester from an aromatic hydroxy compound, carbon monoxide and oxygen as the

feed materials, with a high stability for a long time and at a high reaction rate.

Constitution

A method for manufacturing an aromatic ester, characterized by the following facts: the aromatic ester is manufactured from an aromatic hydroxy compound, carbon monoxide, and oxygen as the feed materials; in the reaction system, there exist the following three types of catalysts: (A) one or several types selected from palladium and palladium compounds, (B) one or several types selected from cerium and cobalt compounds bonded with tropolonato anions, and (C) one or several types selected from halogenated quaternary onium and alkali metal halides.

Effect

According to the method of this invention, the desired carbonic acid ester can be manufactured with a high stability for a long time and at a high reaction rate.

//insert figure//

Claims

1. A method for manufacturing an aromatic ester, characterized by the following facts: the aromatic ester is manufactured from an aromatic hydroxy compound, carbon monoxide, and oxygen as the feed materials; in the reaction system, there exist the following three types of catalysts: (A) one or several types selected from palladium and palladium compounds (referred to as component (A) hereinafter), (B) one or several types selected from cerium and cobalt compounds bonded with at least one molecule of tropolonato anion represented by the following formula (I) (referred to as component (B) hereinafter), and (C)

one or several types selected from halogenated quaternary onium and alkali metal halides (referred to as component (C) hereinafter);

[Structure 1]

/(I) [see orig. p. 2]/

(in formula (I), R^1 - R^5 represent substituents selected independently from hydrogen atom and C1-20 alkyl groups).

2. The method described in Claim 1, characterized by the fact that component (A) is selected from palladium, palladium acetate and bis(tropolonato) palladium carried on activated carbon.

3. The method described in Claim 1, characterized by the fact that for the tropolonato anion represented by formula (I) of component (B), R^1 - R^5 are hydrogen atoms.

4. The manufacturing method of the aromatic carbonic acid ester described in Claim 1, characterized by the fact that in the tropolonato anion represented by formula (I) of component (B), R^1 , R^3 , R^4 , and R^5 represent hydrogen atoms, and R^2 represents an isopropyl group.

5. The method described in Claim 1, characterized by the fact that component (B) is the cerium compound of tris(tropolonato) cerium or tetrakis(tropolonato) cerium.

6. The method described in Claim 1, characterized by the fact that component (B) is tris(4-isopropyltropolonato) cerium or tetrakis(4-isopropyltropolonato) cerium.
7. The method described in Claim 1, characterized by the fact that component (B) is bis(tropolonato) cobalt.
8. The method described in Claim 1, characterized by the fact that component (C) is tetrabutylammonium bromide or bis(triphenylphosphoranylidene)ammonium bromide.
9. The method described in Claim 1, characterized by the fact that component (C) is cerium chloride.
10. The method described in Claim 1, characterized by the fact that the molar ratio of component (A) to the aromatic hydroxy compound is 10^{-3} to 10^{-6} .
11. The method described in Claim 1, characterized by the fact that for the cerium and cobalt compounds as component (B), the molar ratio of the metal elements in component (B) to the metal elements in component (A) is in the range of 10^{-2} to 10^2 .
12. The method described in Claim 1, characterized by the fact that for component (C), the molar ratio of the metal elements of component (C) to the metal elements of component (A) is in the range of 10^{-1} - 10^3 .

Detailed explanation of the invention

[0001]

Industrial application field

This invention pertains to a method for manufacturing an aromatic carbonic acid ester. More specifically, this invention

pertains to an industrially favorable manufacturing method of an aromatic carbonic acid ester using a prescribed catalyst system.

[0002]

Prior art

The aromatic carbonic acid ester, in particular, diphenyl carbonate, is useful when used as an intermediate body for manufacturing polycarbonate, or as an intermediate body or solvent for manufacturing medicines, agrochemicals, dyes, etc. In the prior art, as the method for manufacturing an aromatic carbonic acid ester, reaction between an aromatic hydroxy compound and phosgene is used. However, phosgene is highly toxic. Consequently, this method is undesired. As a method which does not use phosgene, a method has been proposed in which the aromatic carbonic acid ester is manufactured directly from an aromatic hydroxy compound, carbon monoxide, and oxygen. When the latter method is used to manufacture an aromatic carbonic acid ester, a catalyst is usually used. Various manufacturing methods using catalysts have been proposed.

[0003]

For example, the following methods have been proposed: the method disclosed in Japanese Kokoku Patent No. Sho 56[1981]-38144, in which a palladium compound, compounds containing metals in groups IIIA, IVA, VA, VIA, IB, IIB, VIB, and VIIB of the periodical table, and bases are used; the method disclosed in Japanese Kokoku Patent No. Sho 56[1981]-38145, in

which a palladium compound, a manganese or cobalt complex, a base, and a drying agent are used; the method disclosed in Japanese Kokai Patent Application No. Hei 1[1989]-165551, in which a palladium compound, an iodine compound, and zeolites are used; the method disclosed in Japanese Kokai Patent Application No. Hei 2[1990]-104564, in which a palladium compound, a di- or trivalent manganese compound, tetraalkylammonium halide, and quinones are used; the method disclosed in Japanese Kokai Patent Application No. Hei 2[1990]-142754, in which a palladium compound, a cobalt compound, tetraalkylammonium halide, and quinones are used; etc.

[0004]

There are also the following methods: the method disclosed in Japanese Kokai Patent Application No. Hei 5[1993]-25095, in which a cobalt compound, a halide, and a basic compound are used; the method disclosed in Japanese Kokai Patent Application No. Hei 5[1993]-39247, in which a palladium compound, a copper compound, quinones, and onium halide are used; the method disclosed in Japanese Kokai Patent Application No. Hei 5[1993]-58961, in which one or several types of palladium and palladium compounds, a cobalt compound, and an alkali metal halide are used; the method disclosed in Japanese Kokai Patent Application No. Hei 5[1993]-97775, in which the catalyst used is prepared from a palladium compound, a quaternary ammonium salt, one type of metal auxiliary catalyst selected from cobalt, iron, cerium, manganese, molybdenum, samarium, vanadium, chromium, and copper, as well as an organic auxiliary catalyst selected from

aromatic ketone, aliphatic ketone, and aromatic polycyclic hydrocarbon; etc.

[0005]

Also, there are the following methods: the method disclosed in Japanese Kokai Patent Application No. Hei 6[1994]-9505, in which a palladium compound, a cerium compound, and a quaternary ammonium salt are used; the method disclosed in Japanese Kokai Patent Application No. Hei 6[1994]-41020, in which a metal auxiliary catalyst selected from palladium compounds, manganese, cobalt, and copper and a nitrile compound are used; the method disclosed in Japanese Kokai Patent Application No. Hei 6[1994]-172268, in which a palladium compound, 5-coordinated cobalt complex, and a quaternary onium salt are used; the method disclosed in Japanese Kokai Patent Application No. Hei 6[1994]-172269, in which an inorganic auxiliary catalyst selected from palladium compounds, cobalt, manganese, and copper, a quaternary onium salt, terpyridine, and other organic cocatalyst are used; etc.

Problems to be solved by the invention

[0006]

The present inventors performed additional tests in which phenol was used as the base material and a conventional metal auxiliary catalyst was used. It was found that for all of these catalyst systems, after a long period of use, the production rate of diphenyl carbonate as the target product decreases. It

11
is believed that this is due to the decrease in the catalytic activity.

[0007]

The purpose of this invention is to provide an industrially preferable method for manufacturing an aromatic ester from an aromatic hydroxy compound, carbon monoxide and oxygen as the feed materials, with high stability over a long time and at a high reaction rate.

[0008]

Means to solve the problems

In order to solve the aforementioned problems, the invention described in Claim 1 provides a method for manufacturing an aromatic ester, characterized by the following facts: the aromatic ester is manufactured from an aromatic hydroxy compound, carbon monoxide, and oxygen as the feed materials; in the reaction system, there exist the following three types of catalysts: (A) one or several types selected from palladium and palladium compounds (referred to as component (A) hereinafter), (B) one or several types selected from cerium and cobalt compounds bonded with at least one molecule of tropolonato anion represented by the following formula (I) (referred to as component (B) hereinafter),

[0003]

[Structure 2]

/(I) [see orig. p. 3]/

[0010]

(In formula (I), R^1 - R^5 represent substituents selected independently from hydrogen atoms and C1-20 alkyl groups.) and (C) one or several types selected from halogenated quaternary onium and alkali metal halides (referred to as component (C) hereinafter).

[0011]

Detailed explanation of the invention

1. About the feed materials

According to this invention, the feed materials include (1) an aromatic hydroxy compound, (2) carbon monoxide, and (3)

oxygen. In the following, explanation will be given on these feed materials.

[0012]

(1) Aromatic hydroxy compound

The aromatic hydroxy compound used in this invention refers to an aromatic monohydroxy compound and aromatic polyhydroxy compound. Examples include phenol; cresol, xlenol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol, methoxyphenol, ethoxyphenol, chlorophenol, dichlorophenol, bromophenol, dibromophenol, and other substituted phenols and their isomers; naphthol, methylnaphthol, ethylnaphthol, chloronaphthol, bromonaphthol, and other substituted naphthols and their isomers; 2,2-bis(4-hydroxyphenyl)propane, and various other types of bisphenols; various types of hetero-substituted aromatic hydroxy compounds and their isomers, as well as their substituted forms with alkyl, halogen, etc., as substituents. Among them, phenol is particularly preferred.

[0013]

(2) Carbon monoxide

The type of carbon monoxide used in this invention may be either high-purity carbon monoxide or carbon monoxide diluted by air, argon, carbon dioxide, and other gases free of adverse effects on the reaction.

(3) Oxygen

The type of oxygen used in this invention may be either high-purity oxygen or oxygen diluted by air, nitrogen, argon, carbon dioxide, and other gases free of adverse effects on the reaction.

[0014]

2. Catalyst

In the method of this invention, a prescribed type of catalyst is used. The catalyst used in this invention contains the following listed components (A)-(C). Each component contains one or several types selected. The various components are combined for use in the reaction system. In the following, explanation will be given on these three types of components.

[0015]

Component (A)

Component (A) refers to one or several types selected from palladium and palladium compounds.

In addition to palladium metal, the feed materials for component (A) also include inorganic salts, organic acid salts, complexes, etc., of palladium. Examples of the inorganic salts of palladium include palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate, etc. Examples of the organic acid salts of palladium include

palladium acetate, palladium oxalate, acetylacetonopalladium (II), $\text{Pd}(\text{trop})_2$ (where trop stands for tropolonato), etc.

[0016]

The palladium complexes refer to those formed by coordinating carbon monoxide, nitriles, amines, phosphines, olefins, etc., on palladium. Examples include $\text{PdCl}_2(\text{PhCN})_2$ (where Ph stands for phenyl group),

//[a][see orig. p. 4]//

(where DBA stands for dibenzylidene acetone),

//[b][see orig. p. 4]//

etc., as well as mixtures of compounds and palladium that can form these complexes in the reaction system.

[0017]

The aforementioned complexes may be prepared easily using the conventional method, without using a special method, from palladium chloride or palladium acetate as the feed material and by means of reaction under mild conditions in the presence of ligands.

[0018]

It is also possible to have component (A) carried on a certain carrier. Examples of the carriers that may be used in this case include activated carbon, graphite, alumina, silica, alumina-silica, diatomaceous earth, asphalt, calcium silicate, zeolite, aluminosilicate, magnesia, titania, zirconia, cerium oxide, ion-exchange resin, polyvinylpyridine, etc. The conventional method may be adopted to carry component (A) on the carrier.

[0019]

As component (A), one or several types selected from the group of component (A) are used. When the aromatic carbonic acid ester is manufactured using this invention, from the viewpoint of economy and reaction rate, the amount of component (A) present in the reaction system as elemental metal with respect to the aromatic hydroxy compound as the feed material is preferably in the range of 10^{-2} to 10^{-7} , or more preferably in the range of 10^{-3} to 10^{-6} .

[0020]

Component (B)

As component (B), one or several types selected from the cerium compounds and cobalt compounds bonded with at least one molecule of tropolonato represented by said formula (I) may be used. Examples of the alkyl groups in said formula (I) include

methyl group, ethyl group, n-propyl group, isopropyl group, butyl group, hexyl group, octyl group, 2-ethylhexyl group, etc.

[0021]

Examples of the cerium compounds and cobalt compounds for preparing component (B) include inorganic salts, organic acid salts, complexes, etc. Examples of the inorganic salts include chlorides, bromides, sulfates, nitrates, etc. Examples of the organic acid salts include acetate, oxalate, etc. Examples of the complexes include acetyl acetonate salt, as well as compounds prepared by coordinating carbon monoxide, nitriles, amines, olefins, etc., on cerium and cobalt.

[0022]

The tropolonato metal as component (B) may be prepared using the conventional method (for example, the method described by E.L. Muetterties, C. M. Wright, J. Am. Chem. Soc. 87, 4706 (1965), etc.), in which a metal nitrate salt and tropolones are made to react with each other in theoretical amounts in methanol or other polar solvents. From the aforementioned metal salts and tropolones, it is possible to manufacture the desired tropolonato metal in the reaction system. In this case, as needed, it is possible to add alkali metal hydroxides, carbonates, tropolonato salts, etc., as well as ammonia, trialkylamine, and other bases or their tropolonato salts, etc., into the reaction system so as to promote formation of the tropolonato metal.

[0023]

It is possible to replace the aforementioned cerium or cobalt compound with a tropolonato [group] bonded to it by the corresponding cerium or cobalt compound that can form the aforementioned compound in the reaction system and the corresponding tropolone compound in the reaction system at the same time. In addition, when bis(tropolonato)palladium or the like is used as the palladium compound as component (A), there is no need to add the aforementioned tropolone compound.

[0024]

Examples of the cerium compounds among the compounds corresponding to component (B) include tris(tropolonato)cerium, tetrakis(tropolonato)cerium, etc. Examples of the cobalt compounds include bis(tropolonato)cobalt, tris(tropolonato)cobalt, etc.

[0025]

As component (B), one or several types selected from the group of the compounds of component (B) are used. When the aromatic carbonic acid ester is manufactured using this invention, the amount of component (B) present in the reaction system may be at any ratio to component (A). For the metal elements of component (B), the molar ratio to the metal elements of component (A) is preferably in the range of 10^{-2} to 10^2 . If the amount of component (B) is too small or too large, the yield of the target product decreases, and this is undesired. In

particular, the range of 10^{-1} to 10 is preferred among the aforementioned molar ratio range.

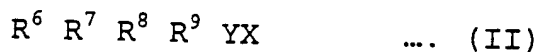
[0026]

Component (C)

Component (C) refers to one or several types selected from (c-1) halogenated quaternary onium compounds and (c-2) alkali metal halides. (c-1) halogenated quaternary onium compounds that can be used in this invention refer to the compounds represented by the following formula (II).

[0027]

[Structure 3]



[0028]

In formula (II), Y represents elemental N or elemental P; X represents halogen atoms of F, Cl, Br, I; R^6 - R^9 represent C1-8 alkyl groups or C6-12 aryl groups, such as methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, octyl group, cyclohexyl group, as well as phenyl group, tolyl group, xylyl group, naphthyl group, etc. They [R^6 - R^9] may be identical or different from each other. Also, R^6 and R^7 or R^8 and R^9 may combine to represent a divalent group of $-(CH_2)_n-$, where n is an integer in the range of 2-7. In addition to the compounds

represented by said formula (II), it is also possible to use bis(triphenylphosphoranylidene)ammonium halides as component (C).

[0029]

Examples include tetra-n-butylammonium bromide, tetraphenylphosphonium bromide, bis(triphenylphosphoranylidene)ammonium bromide, etc. Examples of (c-2) alkali metal halides that can be used in this invention include lithium chloride, sodium chloride, potassium chloride, rubidium chloride, cerium chloride, lithium bromide, sodium bromide, rubidium bromide, cerium bromide, etc.

[0030]

As far as the amount of component (C) ((c-1) and/or (c-2)) used in the reaction is concerned, if no component (C) is present and only components (A) and (B) are present, no catalytic activity is displayed. Then, as the molar ratio of component (C) is increased, the catalytic activity increases almost linearly. Of course, when the amount of component (C) is too much, the catalytic activity becomes saturated, and this is undesired from the viewpoint of economy. For component (C), one or several types selected from the group of component (C) are used. According to the experiment performed by the present inventors, the molar ratio of the metal elements in component (C) to the metal elements of component (A) should be in the range of 10^{-1} - 10^3 , or preferably in the range of 1 - 10^2 , or more preferably in the range of 1 - 50 .

[0031]

3. Reaction conditions

The reaction is carried out as follows. The aforementioned aromatic hydroxy compound and compounds of components (A)-(C) as catalyst are preloaded in a reactor, and a solvent may be added to the reactor. Then, carbon monoxide and oxygen are fed under pressure into the reactor, and the content is well stirred while heated. Examples of the reactors that may be used include a tubular reactor, complete mixing reactor, fluidized-bed reactor, fixed-bed reactor, trickle-bed reactor, etc. The reaction may be carried out in any of batch type, semicontinuous type, and continuous type.

[0032]

The total pressure (absolute pressure) during reaction should be in the range of 0.1-50 MPa, or preferably in the range of 0.1-25 MPa. From the viewpoint of safety, the ratio of carbon monoxide and oxygen should be selected out of the range of explosion. The reaction temperature should be in the range of 20-300°C, or preferably in the range of 80-250°C. The reaction time depends on the composition of the feed materials, reaction pressure, reaction temperature, the composition of the catalyst in use, and other reaction conditions.

[0033]

The solvent used in the reaction is an inert solvent. Examples of inactive solvents that may be used include hexane, heptane, cyclohexane, benzene, toluene, xylene, methylene chloride, chloroform, chlorobenzene, diethyl ether, diphenyl ether, tetrahydrofuran, dioxane, acetonitrile, etc. Also, during the aforementioned reaction, it is also possible to add the following organic additives commonly used for the conventional catalyst system, such as hydroquinone and other aromatic diols, as well as their oxidation products, that is, quinones, amines.

[0034]

Application examples

In the following, this invention will be explained in more detail with reference to application examples and comparative examples. As long as the range of this invention is observed, this invention is not limited to these application examples. The catalysts used in the following examples are commercially available or prepared using the following methods.

[0035]

Component (A):

(A-1) 2% Pd/activated carbon: product of N. E. Chemcat Co., Ltd.
[transliteration]

(A-2) $\text{Pd}(\text{OAc})_2$ (=palladium acetate): product of N. E. Chemcat Co., Ltd.

(A-3) 9% Cs_2PdCl_4 /activated carbon

PdCl_2 and CsCl (commercially available) in a molar ratio of 1:2 were dissolved in water to form an aqueous solution. Afterwards, water was removed by distillation under reduced pressure to form Cs_2PdCl_4 . A calculated amount of the powder of activated carbon (Tako P [transliteration], product of Nimura Chemical Co., Ltd.) was added into the brown aqueous Cs_2PdCl_4 solution, and the mixture was stirred for about 30 min until coloration of the aqueous solution occurred. The mixture was filtered and hydrazine was added to the filtrate. As no precipitate of Pd was formed in the water, all of Cs_2PdCl_4 was adsorbed and carried on the activated carbon. The catalyst carried on the activated carbon was dried for 5 h under vacuum at 70°C.

[0036]

(A-4) $\text{Pd}(\text{trop})_2$ (=bis(tropolonato)palladium)

2.2-Eq aqueous tropolone solution (product of Lancaster Co.) were added to 3N saturated aqueous Na_2CO_3 solution to obtain a yellow aqueous solution. 1N Na_2PdCl_4 was added to the aqueous solution, and the mixture was stirred, forming a precipitate of bright-yellow color. The mixture was stirred at room temperature for 1 h and filtered. The solid was washed with water, forming a solid of orange color. The solid was dissolved in chloroform, and, in order to remove the moisture, a portion of chloroform was distilled off until no turbidity was observed for the

distillate. The obtained chloroform solution was concentrated to form the target (complex) crystal of a brick-like [sic] color.

(A-5) 5% Pd/activated carbon: product of N. E. Chemcat Co., Ltd.

[0037]

Component (B):

(B-1) $\text{Ce}(\text{trop})_4$ (=tetrakis(tropolonato)cerium)

A 3.2-Eq tropolonato solution was added to ethanol solution of $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, so that the color of the solution turned pink. While the solution was stirred at 50°C for 30 min, black crystals were formed. After the crystals were filtered out and washed with ethanol, they were dried under low pressure to form the desired (complex) crystals.

[0038]

(B-2) $\text{Ce}(4\text{-iPr-trop})_4$ (=tetrakis(4-isopropyltropolonato)cerium)

$(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ was dissolved in a small amount of 5% aqueous H_2SO_4 solution. A 4-Eq 4-isopropyltropolone solution in methanol/water mixture (with a mixing ratio by volume of 4:3) was added, and the dark-brown oil-like component was isolated. After adding concentrated sulfuric acid to said aqueous solution to make it acutely acidic, the inclined filtration method was adopted to isolate the oil-like substance, which was then washed with water. The obtained oil-like substance was dissolved in

chloroform and was dried with MgSO_4 , forming the desired (complex) as a brown solid.

[0039]

(B-3) $\text{Ce}(\text{trop})_3$ (=tris(tropolonato)cerium)

The operation was performed in the same way as in the aforementioned manufacturing example of (b-1) $\text{Ce}(\text{trop})_4$, except that an excess amount of triethylamine was added to the reaction system to form the target (complex).

(B-4) $\text{Ce}(\text{OAc})_3 \cdot \text{H}_2\text{O}$: Guaranteed grade, product of Wako Pure Chemical Industries, Ltd.

(B-5) $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$: Guaranteed grade, product of Wako Pure Chemical Industries, Ltd.

[0040]

(B-6) $\text{Ce}(\text{trop})$ [sic; $\text{Cs}(\text{trop})$] (=tropolonato cesium)

1-Eq tropolone (product of Lancaster Co.) was added to ethanol solution of cesium hydroxide (guaranteed grade, product of Wako Pure Chemical Industries, Ltd.) to form a homogeneous solution. The solution was stirred at room temperature for 1 h, and flake-shaped crystals were deposited. The crystals were filtered out and washed with cold ethanol, followed by drying under low pressure to form the target substance.

[0041]

(B-7) $\text{Co}(\text{trop})_2$ (=bis (tropolonato)cobalt)

2-Eq tropolone (product of Lancaster Co.) were added to 2-Eq aqueous Na_2CO_3 solution, and then 1-Eq aqueous $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was added to the above solution to form a brick-colored precipitate. The precipitate was filtered out and washed with water, followed by drying under low pressure to form the target substance (complex).

(B-8) $\text{Co}(\text{OAc})_2$ (=cobalt acetate): Guaranteed grade, product of Wako Pure Chemical Industries, Ltd.

[0042]

Component C

(C-1) CsCl : Guaranteed grade, product of Wako Pure Chemical Industries, Ltd.

(C-2) $n\text{-Bu}_4\text{NBr}$ (=tetra-n-butylammonium bromide): Guaranteed grade, product of Wako Pure Chemical Industries, Ltd.

(C-3) PPNCl (=bis(triphenylphosphoranylidene)ammonium chloride): product of Aldrich Co.

[0043]

(C-4) Ph_4PCl (=tetraphenylphosphonium chloride): Guaranteed grade, product of Wako Pure Chemical Industries, Ltd.

(C-5) PPNBr (=bis(triphenylphosphoranylidene)ammonium bromide)

Said PPNCl , and NaBr in amount of 70 Eq, were dissolved in boiling water to form a saturated solution. After cooling, a white solid was formed. The white solid was dissolved in boiling water to form a saturated solution, and was cooled to form a white solid again. This recrystallization operation was repeated 4 times, forming a white solid of PPNBr .

[0044]

Application Examples 1-13

3.01 g (32 mmol) phenol, 0.012 mg-atom component (A) (palladium compound) and 0.012 mg-atom component (B) (cerium component) with compositions listed in Table I and prepared using the method described in (1) in the above, and 0.24 mmol component (C) (halide) were loaded in a 40-mL autoclave made of Hastelloy and equipped with a reflux cooler, agitator, heating jacket, thermometer, and auxiliary agent inlet. After the interior of the reaction system was substituted with carbon monoxide, carbon monoxide at 6 MPa and dry air under pressure listed in Table I were introduced at room temperature into the reactor, while the content was stirred at 100°C for a duration listed in Table I to carry out the reaction.

[0045]

After the reaction ended in a prescribed time, the vapor-phase sample and liquid-phase sample were collected. For each sample, gas chromatography was performed as quantitative analysis to calculate the yield of diphenyl carbonate and the turnover number. The results are listed in Table I. Also, in Application Examples 7 and 9, activated carbon was added to form Pd/activated carbon in the reaction system. In Application Example 13, (B-6) was added to form $\text{Ce}(\text{trop})_3$ in the reaction system.

[0046]

Table I

. //insert, p. 7//

Key: 1	No.
2	Item

- 3 Component (A) palladium compound .
 - 4 Component (B) cerium compound
 - 5 Component (C) halide
 - 6 Additive
 - 7 Dry air
 - 8 Reaction time (h)
 - 9 Yield of diphenyl carbonate (%) (turnover number)
 - 10 Application Example
 - 11 Activated carbon
 - 12 The abbreviations listed in Table I are defined as follows:
- Pd(OAc)₂: palladium acetate
 - Ce(trop)₄: tetrakis(tropolonato)cerium
 - Ce(trop)₃: tris(tropolonato)cerium
 - Cs(trop): tropolonato cesium
 - PPNCl: bis(triphenylphosphoranylidene) ammonium chloride
 - Ph₄PCl: tetraphenylphosphonium chloride
 - PPNBr: bis(triphenylphosphoranylidene) ammonium bromide
 - Turnover No.: diphenyl carbonate formed (mol)/palladium (mg-atom)
 - Pd(trop)₂: bis(tropolonato)palladium
 - Ce(4-i Pr-trop)₄: tetrakis(4-isopropyltropolonato)cerium
 - Ce(OAc)₃·H₂O: cerium acetate hydrate
 - n-Bu₄NBr: tetra-n-butylammonium bromide

[0047]

From Table I, the following features can be observed. In the reaction system, when there exists the three types of catalysts that meet the requirement presented in Claim 1, even when the types of the three catalysts in combination, the pressure of the dry air applied in the reactor (see Application Examples 1 and 2), reaction time, etc., are changed (see

Application Example 13), the yield of diphenyl carbonate and the turnover number of diphenyl carbonate clearly become higher.

[0048]

Application Example 14

In the same reaction container as that used in Application Example 1, 3.01 g (32 mmol) phenol, 0.012 mg-atom said (A-5), 0.012 mg-atom (B-7), and 0.24 mg-atom said (C-1) were loaded. After the interior of the reaction system was substituted with carbon monoxide, carbon monoxide at 4 MPa and dry air at 2 MPa were introduced at room temperature into the reactor, while the content was stirred at 100°C for 1 h to perform the reaction. After the reaction came to an end, the vapor-phase sample and liquid-phase sample were collected. For each sample, gas chromatography was performed as quantitative analysis to calculate the yield of diphenyl carbonate and the turnover number. The results are listed in Table II.

[0049]

Comparative Example 1

In the same reaction container as that used in Application Example 14, 3.01 g (32 mmol) phenol, 0.012 mg-atom said (A-5), 0.012 mg-atom (B-8), and 0.24 mg-atom said (C-1) were loaded. Then, reaction was carried out in the same way as in Application Example 14. After the reaction ended, the vapor-phase sample and liquid-phase sample were collected. For each sample, gas

chromatography was performed as quantitative analysis to calculate the yield of diphenyl carbonate and the turnover number. The results are listed in Table II.

[0050]

Table II

//insert p. 8//

Key: 1 No.
2 Item
3 Component (B)
4 Yield of diphenyl carbonate
5 Turnover number
6 Application Example
7 Comparative Example
8 The abbreviations listed in Table II are defined as follows:
Co(trop)₂: bistropolonatocobalt
Co(OAc)₂: cobalt acetate
The turnover number in Table II has the same meaning as that in Table I.

[0051]

From Table II, it can be seen that in the reaction system, when there exists the three types of catalysts that meet the requirement presented in Claim 1, the yield of diphenyl carbonate and the turnover number of diphenyl carbonate clearly become higher. On the other hand, when the combination of the compounds fails to meet the requirement of Claim 1 as described in Comparative Example 1, both the yield of diphenyl carbonate and the turnover number become lower.

[0052]

Application Example 15

100.3 g (1.066 mol) phenol, 2.128 g (0.40 mg-atom) said (A-1), 0.40 mmol said (B-1), and 1.347 g (8 mmol) said (C-1) were loaded in a 300-cc reactor equipped with a reflux cooler, electromagnetic inductive type agitator, electric oven, thermometer, and auxiliary agent inlet shown in Figure 1. After the aforementioned feed materials and catalyst were loaded, the reactor was sealed. On the other hand, in pressure reservoir (1), 6 MPa of carbon monoxide and 1 MPa of dry air were pressed in and mixed to form the reaction gas. By means of pressure adjusting valve (2) and back-pressure valve (11), the reaction gas was made to flow from pressure reservoir (1) through the path of reactor (3), cooler (9), and back-pressure valve (11) at a flow rate of 0.6 dm³/min, while the content in the reactor was stirred and heated at 100°C for reaction.

[0053]

Water [vapor] formed in the progress of the reaction was evacuated from reactor (3) together with the reaction gas, and it was liquefied by cooler (9) and collected by trap (10). By means of this operation, the moisture content in the reaction liquid was maintained at a level of about 1 wt%. In order to monitor the state of progress of the reaction, after each prescribed interval, valve (1) and valve (2) are operated to extract a certain amount of the liquid in the reactor through filter (6) made of Hastelloy. For the extracted liquid, gas chromatography was performed to make quantitative analysis, and to determine the yield of diphenyl carbonate and calculate the turnover number, with results listed in Table III.

[0054]

Comparative Example 2

The reaction was performed in the same way as in Application Example 15, except that the catalyst was changed to that described in (1) above. For the vapor phase and liquid phase obtained after the end of the reaction, gas chromatography was performed to carry out quantitative analysis to determine the yield of diphenyl carbonate and the turnover number. The results are listed in Table III.

[0055]

Table III

//insert p. 9//

Key:	1	No.
	2	Item
	3	Component (B)
	4	Reaction time (h)
	5	Yield of diphenyl carbonate
	6	Turnover number
	7	Application Example

- 8 Comparative Example
9 The abbreviations in Table III are the same as those
in Table I.

[0056]

From Table III, the following features can be seen:

(1) In the reaction system, when there exists the three types of catalysts that meet the requirement presented in Claim 1, the yield of diphenyl carbonate and the turnover number of diphenyl carbonate clearly become higher as the reaction time becomes longer, and an excellent catalytic activity is displayed.

(2) On the other hand, when a compound not needed for this invention is used as component (B), both the yield of diphenyl carbonate and the turnover number become lower than those in Application Example 15.

[0057]

Effect of the invention

This invention has the following effects, and it has a very high value for use in industry.

1. When there exists the three types of catalysts that meet the requirement presented in Claim 1, the desired carbonic acid ester can be manufactured at a high reaction rate and with a high stability over a long time.

2. The combination of the three types of catalysts that meet the requirement of Claim 1 of this invention can display a much higher reaction rate under a low oxygen partial pressure than the conventional catalyst system. Consequently, it is possible to inhibit the side reactions caused by the automatic oxidation of the feed phenol. This is an economic advantage.

3. For the catalytic system made of a combination of the three types of catalysts that meet the requirement of Claim 1 of this invention, as a metal salt with tropolonato coordinated on it is contained, and this salt has a very high thermal stability, there is no pyrolysis of the catalyst when the product and catalyst are isolated by distillation.

Brief description of the figure

Figure 1 is a schematic side view illustrating the reaction device used in Application Example 15 and Comparative Example 2.

Explanation of symbols

- | | |
|----|--------------------|
| 1 | Pressure reservoir |
| 2 | Adjusting valve |
| 3 | Reactor |
| 4 | Agitator |
| 5 | Electric oven |
| 6 | Filter |
| 7 | Valve (1) |
| 8 | Valve (2) |
| 9 | Cooler |
| 10 | Trap |

11 Back-pressure valve

//insert figure 1//

Figure 1

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Translated from Japanese by the Ralph McElroy Co., Custom Division
P.O. Box 4828, Austin, Texas 78765 USA